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Abstract

$BaRuO_3$ based perovskite type catalytic material was synthesized by co-precipitation method and its catalytic activity has been tested for diesel soot oxidation. This material shows high catalytic activity for carbon/soot oxidation reaction with lowering of carbon oxidation temperature by >190 ^oC. The catalytic activity could be due to dissociative adsorption of oxygen on $BaRuO_3$ surface. It is postulated by structural investigations that 120 planes of $BaRuO_3$ can have abundant Ru atoms which, can facilitate the oxygen dissociation. The additional advantage of using Ru in $BaRuO_3$ is the thermal stability of Ru in oxide matrix as well as basicity offered by Ba. These synergetic effects can also be responsible for the high soot/carbon oxidation activity of this perovskite type material, which can be a potential candidate for control of soot emissions from combustion processes and vehicle exhaust.

***Key words**: $BaRuO_3$, perovskite, diesel soot oxidation, vehicular exhaust emission control.*

1. Introduction

Particulate matter (PM) emissions from diesel engines are harmful due to both their chemical composition and particle size [1, 2]. The diesel particulate filter (DPF) has so far been the most potential technological option for the effective control of diesel PM emissions, however, its regeneration possibly at the exhaust temperature appears to be the only but difficult limitation. Although, NOx based catalyst assisted passive regenerative type DPFs have been developed, soot oxidation by oxygen/air remains focus of intense research to avoid the NOx dependency for regeneration. Considerable success has been achieved in development of new catalytic materials and the possible mechanisms for the direct soot oxidation by oxygen [3, 4]. As diesel exhaust temperature is substantially lower than the soot oxidation light-off temperature, development of active catalytic materials is still a challenging issue and demand for the investigations on new catalytic materials. Ruthenium in its metallic, coordinated and oxide forms is a good catalytic material for several reactions of commercial and environmental importance [5, 6]. It is an excellent oxidation catalyst [7]. Nevertheless, its catalytic applications for high temperature oxidation reactions and automobile exhaust treatment could not find much practical success mainly due to its relatively inferior thermal stability. Ruthenium dioxide (RuO_2) has a tendency to get oxidized in to higher oxides, which are of volatile nature at temperature beyond 800^{o}C [8]. This has often been a limitation for its high temperature applications, including catalytic applications. Also, there are very limited tailoring possibilities with RuO_2 to alter its catalytic properties for specific reactions. Ruthenium can be stabilized in ABO_3 type perovskite material structure, which offers good thermal stability as well as catalytic material properties due to its structural and chemical specifications [9].

With more reliable findings on effective dissociative adsorption of oxygen on Ru surface, the interest in catalytic properties of Ru based materials has been rejuvenated for academic as well as practical reasons [10]. $BaRuO_3$, one of the relatively simple and stable Ru based oxides, crystallizes in hexagonal perovskite material structure consisting of face sharing octahedra [11]. The hexagonal $BaRuO_3$ provides an example of the complex oxide based on closed packed stacking of BaO layers of perovskite type material structure. The physical properties of $BaRuO_3$ compound are mainly due to unfilled 4 d level of Ru ions, however, the ionic radii of Ba cation also play a significant role [11]. Presence of ruthenium in 4+ stable oxidation state and possible influence of Ba on the catalytic active Ru makes this compound a potential material for catalytic studies. The properties of ruthenium based perovskite type materials for their catalytic applications have been seldom investigated, although theoretically they can be potential catalytic materials for various reactions including oxidation reactions. We have been successful in development of new and improved methods for the synthesis of lanthanum based perovskite type ruthenate materials, which show high thermal stability and catalytic properties [9, 12-14]. As ruthenium is relatively much cheaper (about 18 times than Pt, 10 times than Pd and 12 times to that of Rh) metal than other Platinum Group Metals (PGM), its use in autho-exhaust emission control can be justified.

In this work, we report the catalytic properties of $BaRuO_3$ type perovskite material with high catalytic activity for carbon/soot oxidation reaction, probably for the first time. It was possible to understand certain structure-property relations through the structural models as well as the chemical composition of this material. The activity and stability results of $BaRuO_3$ can help rejuvenating ruthenium based perovskites for important applications in environmental catalysis.

2. Experimental

2.1. *Synthesis of $BaRuO_3$*

Co-precipitation has been widely used for the synthesis of a large number of perovskites. In the present method, Ba^{2+} and Ru^{3+} precursors were dissolved in deionized water and subsequently mixed together. The mixed metal ion solution was slowly added with constant stirring, to aqueous mixed alkali solution. A mixed alkali solution was prepared by mixing 500 ml each of 1M aqueous ammonium carbonate solution and 500 ml of 1 N aqueous ammonia solution. The precipitate thus obtained was allowed to settle for 5 h followed by filtration and washings with de-ionized water and oven drying at 70 ^{o}C. The resultant mass was heated at 500 ^{o}C for 5 h followed by grinding and further heating at 800 ^{o}C for 6 h.

2.2. *Characterization*

XRD patterns were recorded on a Rigaku Rint-220HF diffractometer, operated at 40 kV and 50 mA with a monochromator and using Cu Kα radiations (λ =0.15418 nm). Indexing of XRD peaks was done, by using JCPDS database for the respective phases. Surface area was measured by nitrogen adsorption method using automatic gas adsorption apparatus BELSORP 28SA (produced by Nippon Bell Co.) and data were evaluated by BET method. The samples were pre-treated at 300 ^{o}C before the nitrogen adsorption experiments. Thermal stability experiments were performed by heating the material at 900 ^{o}C, under air atmospheres and also performed using TGA technique (Rigaku-TAS-200 apparatus) in the same temperature range, mainly to study the possibility of thermal loss by the formation of volatile ruthenium oxides.

2.3. *Catalytic Evaluations*

The synthesized $BaRuO_3$ was evaluated for its carbon/soot oxidation activity following a batch type temperature programmed reaction procedure using activated carbon. 100 mg of carbon-catalyst (ca. 5wt%) mixture was homogenized in an agate lines mortar pestle, pelletized (tight contact condition) and sieved to 20-100 mesh. The pellets were placed in a fixed bed flow reactor

with a programmable heater controller. A gas mixture containing 15 % oxygen was flown with the increasing temperature with a predetermined heating cycle. Gas analysis was carried out using an auto-sampling PC controlled, MTI-P-200, Shimadzu GC system with molecular sieve and Porapak-Q and molecular sieve columns. The activation energy has been estimated by using Ozawa method by proper interpretation of TGA data. The thermo gravimetric analysis experiments were performed under loose contact condition wherein the mixture of soot and catalysts were heated from 35 to 800°C at different heating rates, in air atmosphere. According to the Ozawa Method, the following relationship links the values of the heating rate In (ϕ) with the corresponding values of temperature (T_α) at which a fixed fraction of carbon is burned during each run;

$$\ln(\phi) = 1.052(E/R)(1/T_\alpha) + A$$

Where, A is a constant, E is activation energy (kJ $mole^{-1}$) and R is ideal gas constant (8.314 J/ mole/K) [15, 16]. In this case, TGA experiments were performed using the loose contact method by shaking the mixture of catalyst and carbon (90:10) in a glass bottle for five minutes. This method is often used as a loose contact method for catalytic soot oxidation experiments.

3. Results and discussion

The synthesized $BaRuO_3$ has three crystallographic forms representative of the "hexagonal perovskite". These different forms depending of the pressure parameters, are known as the 9R, 4H and 6H layers. At ambient pressure, $BaRuO_3$ has been found to adopt the 9-layers repeat sequence (chh)3. 9R-$BaRuO_3$ crystallizes in the Rhombohedral space group R-3m (unit cell a = 5.75 A and c=21.60 A). The structure consists of trimers of face sharing octahedra, which are joined via terminal corners to constitute a three-dimensional network [11]. The XRD analysis (Fig. 1) confirms the formation of single phase, crystalline $BaRuO_3$ and infers that $BaRuO_3$ can be easily synthesized by co-precipitation method with good purity and crystallinity. The BET-surface area

result of synthesized $BaRuO_3$ is observed to be 5 m^2/g, which is in the expected range, considering the high synthesis temperature used, leading to sintering of material. The barium and ruthenium contents of the catalyst were determined using ICP-OES technique (Perkin–Elmer, Model Optima 4100DV). Blank experiments were performed throughout the studies and majority of the experiments were repeated thrice and it was observed that the experimental error was within ±2%. The samples were dissolved in acid before the analysis. The $BaRuO_3$ sample was then studied for its thermal stability as RuO_2 suffers thermal loss due to the formation of volatile oxides. The post-heated material shows practically no change in the XRD pattern, thereby confirming the unchanged structure and crystallinity of the material, while practically no weight loss was observed during heating the materials on a TGA machine. It can therefore be inferred that Ru can be thermally stabilized as $BaRuO_3$ in perovskite structure, under the oxidative atmosphere.

3.1. *Catalytic activity*

Diesel particulate (soot) consists of carbon core associated with hydrocarbons including polyaromatic hydrocarbons (PAH) and nitro-PAH, sulfates, water, trace amounts of other metals [17]. The non-catalytic combustion temperature of soot generally exceeds 550 ^oC, however, this depends on various factors. Therefore, model soot/carbons are generally used for laboratory studies, which offer much better reproducibility than the natural soot. The model soot/carbons used in this study are activated carbon (for fixed bed evaluations) with following physicochemical properties: fraction of adsorbed hydrocarbons (5.2%), ash (<0.14%), C (94.2%), H (0.4%), N (0.3%), S (0.5%) and carbon black (Degussa S.A. Printex) for TGA based evaluations.

The carbon oxidation activity results for bare activated carbon using temperature programmed oxidation (TPO) are presented in Fig. 2a. These results suggest that the T_i

160 (Temperature at which carbon oxidation initiated) of the non catalyzed oxidation of carbon starts
161 above 400 ^{o}C and effective soot oxidation was observed only after 540^{o}C with T_f (Temperature at
162 which carbon oxidation completed) at 650 ^{o}C. TPO results for $BaRuO_3$ assisted activated carbon
163 oxidation (Fig. 2b) suggest that the carbon oxidation with $BaRuO_3$ catalyst shows two peaks in
164 the temperature range of 200–480 ^{o}C. This initial oxidation (first peak) can be attributed to the
165 catalytic oxidation of soluble organic fraction (SOF) component, which is an exothermic
166 reaction. The exothermic heat generated during oxidation of SOF fraction also leads to carbon
167 oxidation, especially the carbon part in close contact with catalyst particles. Therefore, the first
168 peak could be correlated to combined effect of SOF oxidation as well as carbon oxidation
169 promoted by exothermic heat of SOF oxidation and that in closer contact with catalyst particles.
170 The second peak appeared at 300 ^{o}C could be due to the release of CO_2 as a result of carbon
171 oxidation without substantial SOF content and with relatively weaker contacts. The T_i and T_f of
172 catalyst assisted soot oxidation were observed to be around 200 ^{o}C and 435 ^{o}C, respectively.
173 These results show decrease in T_i value by about 200 ^{o}C and T_f by 215 ^{o}C with catalyst assisted
174 carbon oxidation as compared to non-catalyzed activated carbon oxidation. Such results confirm
175 high catalytic activity of $BaRuO_3$ in absence of NO_x. Soot oxidation is usually facilitated by
176 presence of NO_2 at low temperatures following the formation of NO oxidation to NO_2. The
177 observed lowering of carbon oxidation temperature in absence of NO_2 is therefore quite
178 significant [18-23], and thus the present $BaRuO_3$ catalyst shows excellent catalytic activity
179 considering it's very low surface area. This observation also support that the micro surface area
180 is not very important in case of oxygen based soot/carbon oxidation considering the fact that
181 both catalyst and a reactant are in solid state. There was practically no CO generation, which is
182 sometimes present as a product of incomplete combustion. The XRD analysis of post-heated

sample at 900 ^{o}C does not show any change as compared to that of original material. This confirms the high thermal stability of $BaRuO_3$, otherwise RuO_2 and Ru metal are well known to show thermal loss at such high temperatures in oxidative atmosphere. Such batch experiments using the air or simulated exhaust flow offer relatively more realistic conditions of catalyst use for DPF (Diesel particulate filter) regeneration as compared to thermo gravimetric analysis (TGA) based evaluations. The activation energy for catalyzed and non-catalyzed reactions was estimated by following the Ozawa method [15-16]. The activation energy values (Table 1) of catalyzed reactions under different conditions unambiguously substantiate the high catalytic activity of $BaRuO_3$ for carbon / soot oxidation using different feed gas mixtures.

A few mechanisms have been proposed for the catalytic soot/carbon oxidation using oxygen/air. Based on our previous extensive studies on soot oxidation reaction [20-23] as well as the kinetic analysis [24], we postulate that dissociative adsorption of oxygen on catalyst surface followed by its reaction with the solid soot/carbon at the soot-catalyst interface could be the possible mechanism for present perovskite composition. With this background, we have attempted the possibility of explaining high activity in relation to surface structure of this material as derived from crystallographic assumptions. Fig. 3 and Fig. 4 illustrate the possible rich oxygen–ruthenium surface chemistry. The ball model derived in the present study shows abundant population of Ru on –120 planes. We decided to study this plane with the hypothesis of needle particles (crystal growth along c axis), which is classically obtained for hexagonal stacking perovskite. Moreover, in case of $BaRuO_3$, there is direct Ru-Ru interaction as compared to that of RuO_2, which may favor dissociative adsorption of oxygen. However, another important factor for the relatively higher activity of $BaRuO_3$ may be the influence of adjacent Ba cation in perovskite structure. The basic character of Ba is expected to weaken the strength of Ru-O bond,

which facilitate the release of adsorbed oxygen. In this way, it is quite possible to explain the excellent catalytic activity of this material, while the material also shows a very important advantage of thermally stabilizing Ru in an oxide matrix.

4. Conclusions

$BaRuO_3$ with perovskite structure can be easily synthesized using co-precipitation method. The catalytic material shows high catalytic activity for soot oxidation reaction as compared to most of the non-PGM (non-platinum group metals) based catalyst reported for direct soot oxidation, while it's activity is also comparable with PGM metal based catalysts. $BaRuO_3$ shows high soot oxidation activity under both flow type reactor conditions as well as TGA. 120 planes of $BaRuO_3$ are postulated to have abundant Ru atoms, which can facilitate the adsorptive dissociation of oxygen. This surface can also provide weak Ru-O interaction due to the presence of Ba, which may facilitate easy release of dissociated oxygen. It is also significant to achieve high thermal stability for ruthenium in an oxide matrix. The present catalytic studies of $BaRuO_3$ therefore suggest for the preparation of other similar metal ruthenates and study of their detailed catalytic and material properties. This metal ruthenate with perovskite structure shows potential for its applications in environmental catalysis. The high thermal stability of $BaRuO_3$ material is quite striking as this has been a major limitation with Ru based catalytic materials.

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Figures:

Fig. 1: XRD Pattern for $BaRuO_3$

Fig. 2a: Temperature Programmed Oxidation results for carbon oxidation: bare activated carbon

Fig. 2b: Temperature Programmed Oxidation Results for carbon oxidation: activated carbon with $BaRuO_3$ catalyst.

Fig. 3: Ball model of the $BaRuO_3$ (-120) surface

Fig. 4: Projection along [010] of the (–120) surface

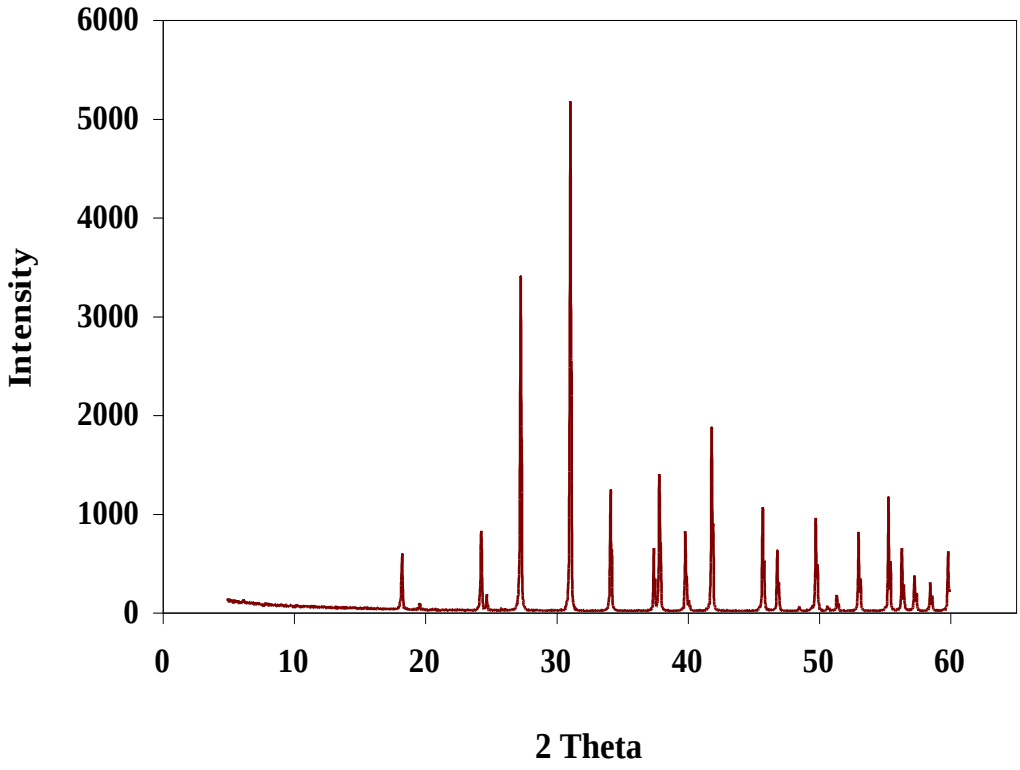
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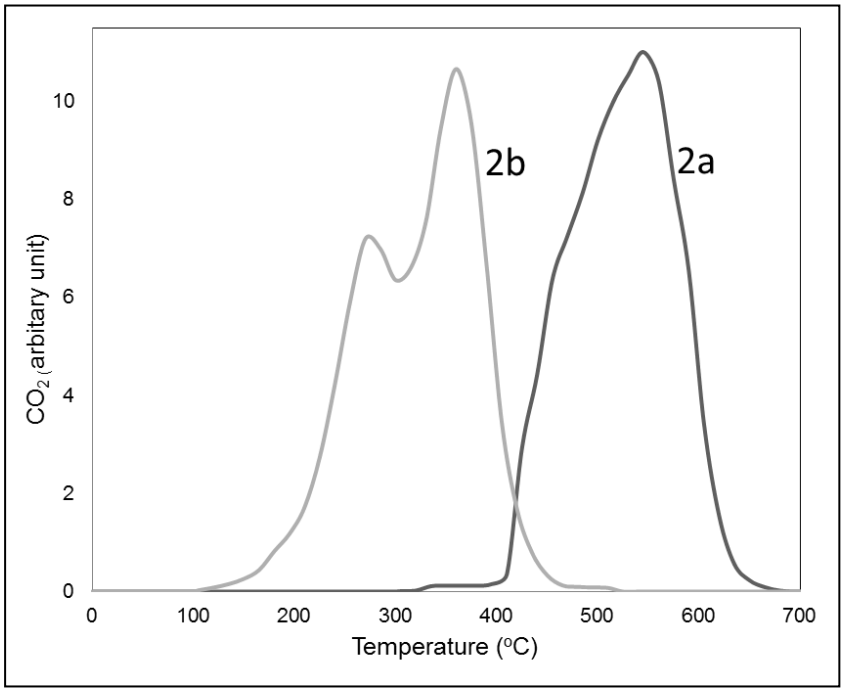
Fig.1


2b
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8
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Temperature (°C)
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Fig. 2a & Fig. 2b

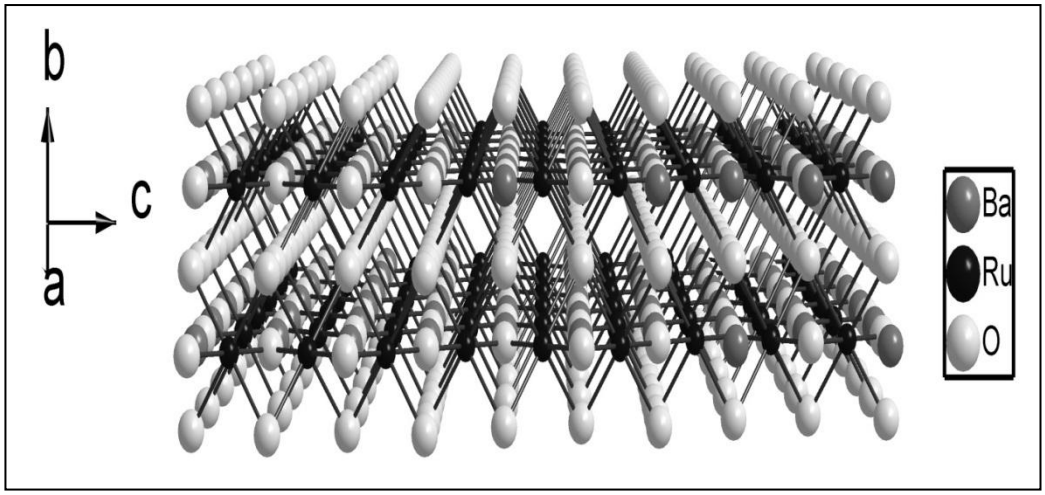

Fig. 3

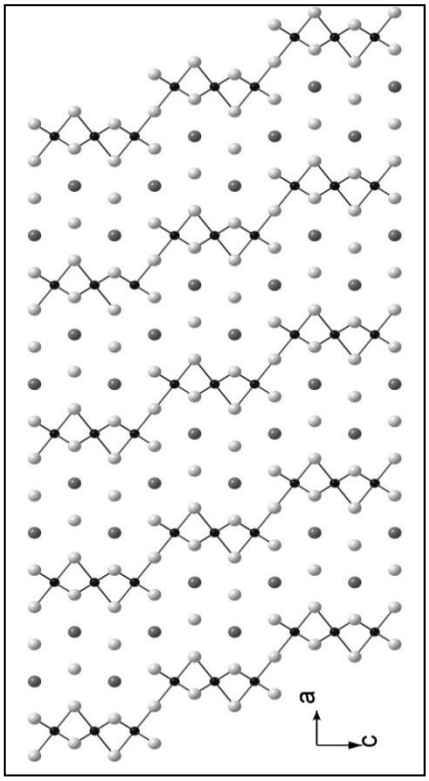

Fig. 4

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Sample	Activation Energy kJ/mol		
Bare carbon black	150 (Air flow)	165 (12%O_2)	160 (12%O_2+10%CO_2)
Carbon black +$BaRuO_3$	120 (Air flow)	135(12%O_2)	130(12%O_2+10%CO_2)

413

414 **Table 1: Activation energy values (Ozawa Plot), kJ/mol**